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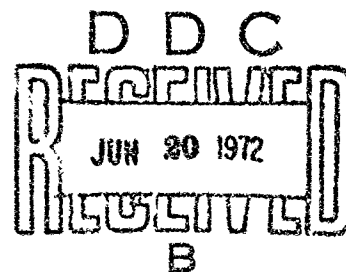
ADMIXTURES FOR CONCRETE

by

Bryant Mather



October 1967



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U. S. Army Engineer Waterways Experiment Station
CORPS OF ENGINEERS

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FOREWORD

Brig. Gen. W. C. Hall, USA (Ret), Editor, The Military Engineer, invited the preparation of technical papers on four subjects relating to the work of the Concrete Division, Waterways Experiment Station. This is one of these. The manuscript was approved for publication by the Office, Chief of Engineers (OCE). The conclusions stated were derived largely from studies sponsored by the OCE under the Civil Works Investigations - Engineering Studies Program.

COL John R. Oswalt, Jr., CE, was Director of the Waterways Experiment Station during the preparation of this paper. Mr. J. B. Tiffany was Technical Director.

Admixtures for Concrete*

by
Bryant Mather**

Any material, other than water, aggregates, and hydraulic cement, used as an ingredient of a concrete or mortar mixture, added to the batch immediately before or during its mixing, is, by definition, an admixture. Such materials, when interground or interblended with the hydraulic cement, are described as "additions" to the cement. The purpose of using an admixture is to make the concrete or mortar to which it is added more suitable for the purpose for which it is used or available at lower cost. An admixture should not be used unless there are benefits to be obtained that are worth the cost of so doing and are benefits that cannot be obtained by other means except at greater cost.

One of the most widely used classes of admixtures is pozzolans. A pozzolan is a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties. Pozzolans are characterized by containing a large proportion of silica in a form that will react with hydroxides. The silica may be present as natural volcanic glass, artificial glass (as in fly ashes), opal (as in diatomaceous earths), or the disordered forms of silica present in many clays and shales.

*Prepared for submission to the Editor, The Military Engineer.

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Pozzolans are used primarily because, by so doing, the cost of suitable concrete for the purposes intended can be produced at lower cost than would be experienced if they were not used. The Corps of Engineers frequently includes in the specifications for its larger projects several alternative compositions for concrete, one of which is that it shall be composed of "portland cement, water, fine and coarse aggregate, and an air-entraining admixture," and, frequently, another is "portland cement and pozzolan, water,...." When this is done, the bids are invited under procedures in which the bidder may bid unit prices and totals either on a given number of barrels of portland cement or an equal solid volume of portland cement and pozzolan, of which 20 to 35 percent of the total is pozzolan, the amount being selected with reference to the properties of the concrete and the available pozzolanic materials. Since this option has been made available, most bidders have elected to use it, and a saving of cost of about \$0.60 per cubic yard of concrete has been realized to the Government.

Admixtures can^{be} and are being used to modify virtually any property that concrete naturally possesses and are also used to impart properties it could not otherwise have. In some cases the effect is to change the time at which the concrete develops a given property to a given degree; in other cases a property is conferred that, without the admixture, could never have been achieved by the concrete mixture.

Admixtures have been used for at least 2000 years. Marcus Vitruvius Pollio in the first century A. D. set forth a specification for mortar that called for well-hydrated lime, marble dust, sand, and water, "to which is added either hog's lard, curdled milk, or blood." In 1967, the National

Renderers Association and the Fats and Proteins Research Foundation were sponsoring a survey of the utility of inedible fats as admixtures for concrete. The two most widely used classes of products employed as admixtures for concrete, organic chemical materials and active mineral powders (Pozzolans), were both known to and used by the Romans in classical times.

Among the effects that are sought by the use of admixtures are the following:

- a. Achievement of an earlier setting time (acceleration).
- b. Delay of setting time (retardation).
- c. Achievement of equal workability with lower water content (water reduction).
- d. Incorporation of a system of entrained air voids in the cement paste (air entrainment).
- e. Removal of excessive amounts of air bubbles from the cement paste (air detrainment).
- f. Reduction of permeability of concrete (permeability reduction).
- g. Inhibition of tendency of embedded metal to corrode (corrosion reduction).

The principal materials used for these purposes are as follows:

- a. Accelerators. The most widely used accelerator is calcium chloride. Other materials which accelerate the hardening of mixtures of portland cement and water include other soluble chlorides; soluble carbonates, silicates, fluosilicates, and hydroxides and some organic compounds such as triethanolamine. Calcium chloride can generally be used safely in amounts up

to 2 percent by weight of the cement. The benefits of such use are greatest in cold weather, and at high temperatures the effects may be detrimental. Calcium chloride should not be used where stray electric currents are to be expected or in prestressed concrete because of its tendency to promote corrosion of steel. It is convenient to make solutions in which one quart contains one pound of calcium chloride.

b. Retarders. All commonly used retarding admixtures are organic chemicals, generally lignosulfonic acid salts or hydroxylated carboxylic acid salts or modifications thereof. At normal temperatures, used in normally recommended amounts, the setting time of concrete may be extended 30 to 50 percent. Greater delays of setting can be obtained by using larger amounts. Retarders are usually used to compensate for the undesired accelerating effects of high placement temperatures, to avoid cold joints, and to avoid undesirable effects of displacements and deflections due to loading of forms and supports by subsequent concrete placement in construction such as composite multispan bridge work.

c. Water reducers. The same basic kinds of materials that are retarders are generally water reducers. Most water reducers are retarders that have been modified to suppress or compensate for their retarding effect. Water reducers are necessary in the production of very high-strength concrete. It is rarely possible to produce concrete that will develop significantly

more than 10,000 psi compressive strength except by the use of a water-cement ratio in the range of 0.30 to 0.35 by weight. If concrete of this water-cement ratio is to have sufficient workability to be placed, the use of a water reducer is generally required. Water reducers may also be used to achieve concretes of any strength at lower cement content.

d. Air-entraining admixtures. The materials used as air-entraining admixtures are those which make foam; they are thus similar to soaps and detergents. They are generally derived from resins, fats, or oils. The primary purpose of air entrainment is to protect the concrete against the damage it may suffer if the paste becomes saturated with water and then freezes. A mature portland-cement paste in which air bubbles are present with a spacing factor of 0.008 in. or less will not be damaged by freezing even if saturated with water. The spacing factor is the average maximum distance from any point in the paste to the nearest air void. With normally used air-entraining admixtures, the air-void spacing factor will be within the correct limits if the amount of air-entraining admixture used is such that the freshly-mixed concrete contains 9% air in the mortar fraction or 5-1/2% air in concrete containing aggregate of 1-1/2-in. maximum size. The amount of air-entraining admixture required to produce the specified air content will be greater at higher temperatures, in mixtures containing larger proportions of fine materials, or when materials are used that tend to adsorb organic materials.

If an acceptable air-entraining admixture is used in an amount such that the proper air content is developed in the freshly mixed concrete, tests have shown that expulsion from the concrete of a large proportion of the total air content by continued vibration does not significantly alter the air-void spacing factor and hence does not destroy the protection furnished against frost damage.

e. Air-detraining admixtures. Cases have been reported in which concrete mixtures made with certain materials, especially certain natural aggregates, contain substantially more entrapped gas bubbles than normal. Such a condition greatly hampers production of air-entrained concrete, since the gas bubbles that are present without any air-entraining admixture are relatively large and ineffective in providing frost resistance. In other cases, it is desired to use a water-reducing or a retarding admixture that also entrains air but not to have entrained air in the concrete. In these and similar cases a material such as tributyl phosphate is used as an air-detraining admixture to dissipate and expel the unwanted bubbles of air or other gas.

f. Permeability reducers. Materials have been marketed as admixtures that have been described as "waterproofers." Many such materials are of the nature of soaps, oil, or resins which are water repellent and may, by this method, retard the wetting

of a concrete or mortar by drops of water that fall on its surface. Most such materials, if employed for this purpose, are used as surface applications to hardened concrete or mortar surfaces. Admixtures have not been found that will prevent the entry of water into concrete or its transmission through concrete. Some admixtures will, however, reduce the permeability of mortars and concrete to water. Permeability reducers are mineral powders that increase the solids content of lean mixtures and, if they are cementitious or pozzolanic, react to produce additional solids after they are incorporated in the concrete.

- g. Corrosion inhibitors. Ferrous metal (iron and steel) embedded in concrete will not rust if the metal is kept completely sealed from access to the external environment and the concrete maintains its normal alkaline state (pH greater than 12). Where the possibility of corrosion arises from insufficient cover of concrete over the steel, this cannot be mitigated by the use of an admixture in the concrete except as the admixture may reduce the permeability of the concrete and hence increase the effective cover. If, however, the possibility of corrosion arises from reduction of the normally protective chemical nature of the concrete, then use of admixtures to retard or inhibit corrosion is a possibility. Among the materials that have been studied are sodium benzoate, calcium lignosulfonate, stannous chloride, and sodium nitrite.

The American Concrete Institute has had a committee on Admixtures since 1943. This committee is assigned the mission to "gather, correlate, and report information on the effect of various admixtures on the properties of concrete and prepare recommended practices for the use of admixtures." The committee's third and latest report was published in November 1963. It contains much additional information on admixtures.

(Jour. Amer. Conc. Inst., Proc., Vol 60, Nov 1963, pp 1481-1524, available from ACI for \$1.00)

In some circles the word "admixture" creates a negative reaction. It seems to be regarded by some that deliberately putting anything into concrete--other than water, aggregates, and portland cement--is adulterating the mixture. Some of those concerned with the marketing of portland cement have tended to foster this impression because of a belief that, since in many cases, the use of admixtures has as one of its benefits the reduction in the unit quantity of cement required per unit volume of concrete, admixtures are competitors of cement. Such is not the case. Any method or material that makes concrete either more widely useful or available at lower cost increases the use of concrete and of cement. The Director of Research of the Portland Cement Association has written: "The impression seems to be fairly widespread that the PCA is against admixtures of every kind. This is simply not so. For nearly two decades we have been advocating air-entrained concrete....air-entraining admixtures are an indispensable part of modern concrete technology. There are circumstances under which accelerators or retarders or water reducers or other admixtures may usefully be employed...We do not recommend indiscriminate use of admixtures....which

renders the concrete less than adequate for its intended purpose....Use without adequate accuracy in batching, without adequate understanding of use and function....will lead to inadequate concrete."